T0 vs Pico de Tres Padres: The first few hours of mixing and oxidation

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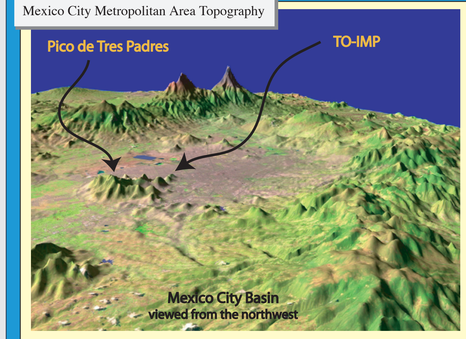
Mexico City Metropolitan Area Topography



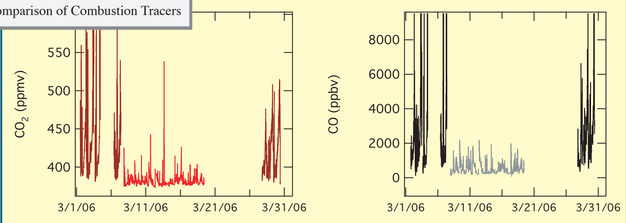
This poster compares a subset of data collected during the MILAGRO 2006 campaign at the T0 Supersite, to a location the Aerodyne Mobile Laboratory was able deploy to located on top of Pico de Tres Padres.

The composition of the trace species in the atmosphere at these two locations indicates that T0 is located among multiple emission sources. The air at Pico de Tres Padres, however, appears to be a reasonably well mixed urban plume with indications that photochemical processing has begun.

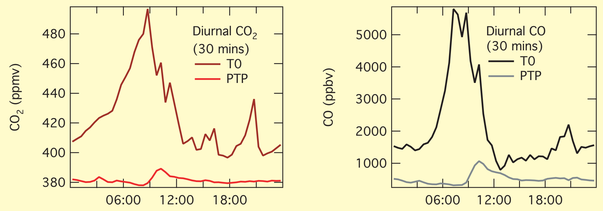
This work is a first look at what analysis avenues may be pursued with this intriguing dataset.

See Zavala et al. poster for addition site info

Comparison of Combustion Tracers



Primary Combustion Traces, CO_2 and CO exhibit very different temporal profiles at the two sites

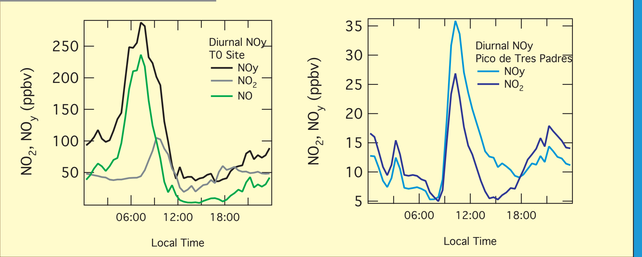


CO Emission Ratio ~ 0.048 - 0.065 or 15-20 CO_2 per CO
2003 Result ~ 0.052-0.085 on-road and at CENICA

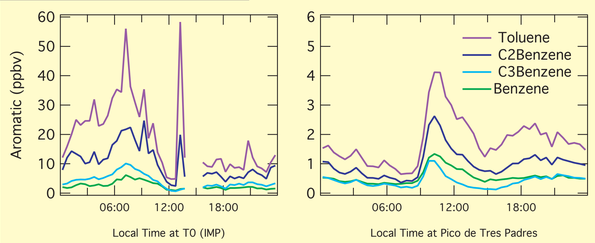
Is the penetration of new automobiles into the MCMA fleet 2003->2006 making a difference in fleet average CO ER?

Fraction of cars with emissions control			
2000	2002	2004	2006
61%	65%	74%	?

Diurnal NO, NO_2 and NO_y site comparison



PTR-MS Benzene, Toluene and other Aromatics



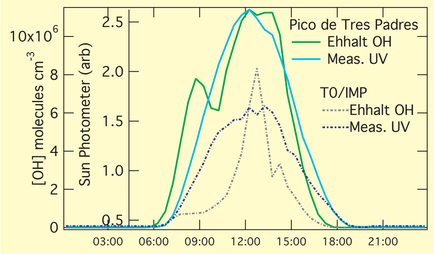
At the Pico de Tres Padres site, the aromatics measured via PTR-MS ~ten times lower
Spikes at T0 are due to solvent emissions -- See poster Knighton et al. poster for more

OH drives daytime oxidation; Without a measurement, can it be estimated?

Ehhalt Parameterization for estimating OH

$$[OH] = 4.1 \times 10^{9}\, j(O^1D)^{0.83}\, j(NO_2)^{0.19}\, \frac{140\,[NO_2] + 1}{0.41\,[NO_2]^2 + 1.7\,[NO_2] + 1}$$

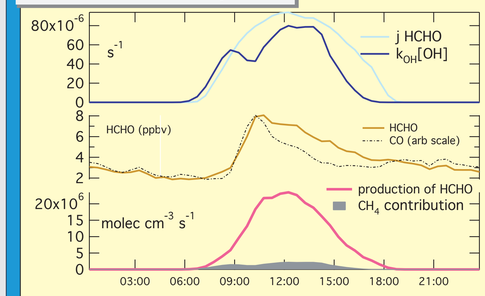
Clear Sky Photolysis Values Calculated by Madronich TUV.exe
(scaled by arbitrary Sun Photometer aka, "Shade Meter")
NO_2 measured using Quantum Cascade Laser Rot/Vib IR



Direct NO emissions at T0/IMP complicate this estimate

The parameterization for OH may not be quantitative, however, these number densities may help estimate the temporal behavior of observed VOC photochemistry

Estimated OH, Measured HCHO, *p*HCHO



Using the Ehhalt parameterization for OH and the 'shade-scaled' clear sky j HCHO the production of HCHO is estimated assuming the measured value is in photochemical steady state

$$p(HCHO) = [HCHO]_{ss} * \{ k_{OH}\,[OH] + j(HCHO) \}$$

Estimating *loss*(HCHO)

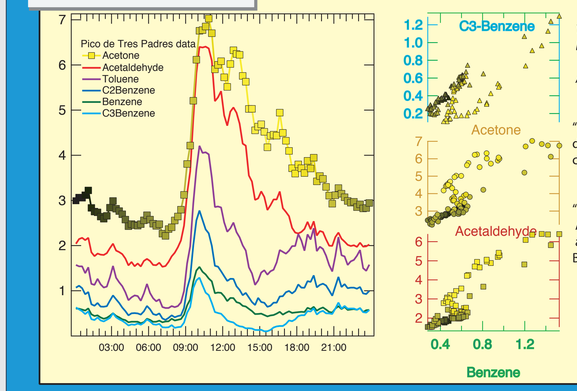
O_2
$OH + HCHO \rightarrow H_2O + HCO \rightarrow HO_2 + CO$

$HCHO + h\nu \rightarrow$ $H_2 + CO$
$H + HCO \rightarrow\rightarrow 2\,HO_2$

k_{OH} (10^{-12} cm^3 molecule^{-1} s^{-1})	
Benzene	1.23
Toluene	5.96
m,p-xylene	18.95
o-xylene	13.70
Ethylbenzene	7.10
1,2-4-trimethylbenz.	32.5
1,3,5-trimethylbenz.	57.5
m-ethyltoluene	19.2
p-ethyltoluene	12.1
o-ethyltoluene	12.1
n-propylbenzene	6.9

Atkinson *J.Phys.Chem* Ref Data **2**,11-216, 1994 & **26**, 215-290, 1997

Evidence of Photochemistry at PTP



Yellow indicates daytime
Black indicates nighttime

All units are ppbv

"Reactant" C3-Benzene is depleted during photo-chemistry relative to Benzene

"Reactant/Product" species, Acetone & Acetaldehyde are enhanced relative to Benzene

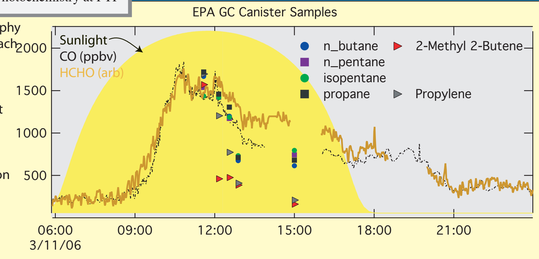
Additional Evidence of Photochemistry at PTP

Evacuated Gas Chromatography canisters were collected at each of the sites.

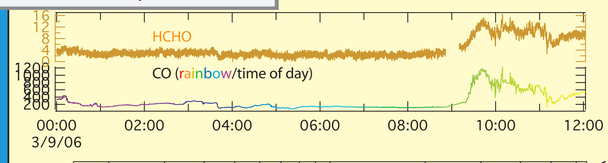
The alkanes are longer lived in the atmosphere than most alkenes

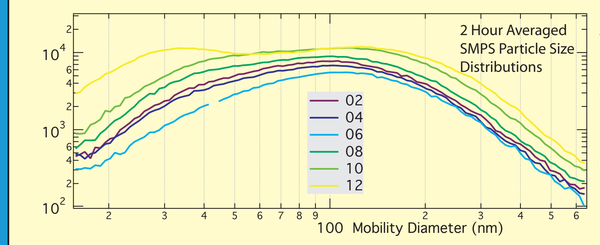
These results futher indicate that during the mid-afternoon photochemistry, alkanes survive while alkenes are depleted.

Additional analysis, adapted from the approach of de Gouw *JGR* **110** D16305 will be conducted



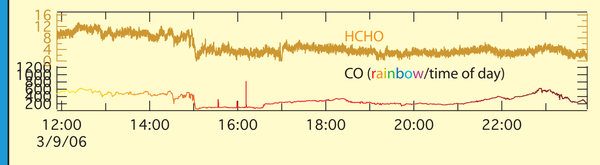
SMPS: Photochemistry and 30 nm mode?

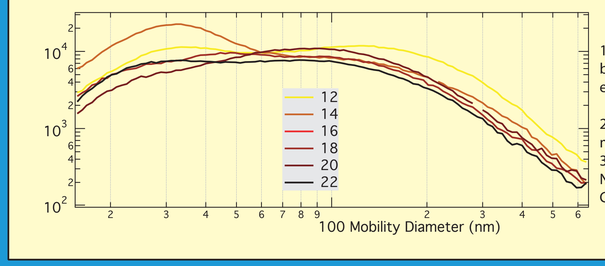




6-8 am, CO indicates fairly 'clean' air
SMPS has lowest integrated number count

10 am - 12 pm SMPS sees large jump in ~ 40 nm & 120 nm modes

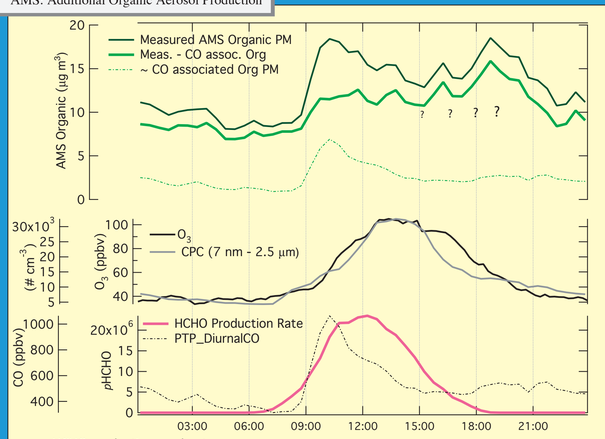




12 - 2 pm large bulge at ~ 30 nm emerges

2 - 4 pm pronounced mode emerges at 30 nm
Note combustion tracer CO decreasing

AMS: Additional Organic Aerosol Production



HCHO production peaks at noon;
O_3 concentration peaks mid afternoon, along with the CPC number count
If a fraction of the measured AMS Organic mass is attributed to direct emissions & prompt SOA, is PTP seeing a secondary aerosol production in the late afternoon and early evening?

Some Future Analysis Efforts

The day to day events and time series will be analyzed in light of the baseline diurnal understanding that has emerged

PTR-MS and GC data will refine photochemical clocks suitable for the Pico de Tres Padres site

FLEXPART back trajectories will be incorporated to examine whether different source profiles can be seen (after accounting for some chemistry along the path)

The AMS size distributions will be examined to corroborate the SMPS observation

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Although portions of this work were reviewed by EPA and approved for presentation, it may not necessarily reflect offical Agency policy.